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Structural and photoluminescent properties of ZrO_2:Tb^{3+} coatings formed by plasma electrolytic oxidation

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ABSTRACT

Tb^{3+} doped ZrO_2 coatings were formed on zirconium substrate by plasma electrolytic oxidation (PEO) in electrolyte containing Tb_4O_7 powder. The evolution morphology, chemical composition, and crystalline structure of formed coatings as a function of PEO time are probed by scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction. The concentration of Tb incorporated into coatings increases with the time of PEO processing. Obtained coatings are crystallized and composed of monoclinic and tetragonal phases of ZrO_2. The ratio of monoclinic and tetragonal phases, as well as crystallite size, is controlled by PEO time and concentration of Tb in coatings. Photoluminescence (PL) emission spectra of Tb doped ZrO_2 coatings feature two distinct regions. The first region is related to ZrO_2 PL band with a maximum positioned at about 490 nm, while the second region features several sharp emission bands which can be attributed to f-f transitions of Tb^{3+} from excited level $^5D_4$ to lower levels ^7F_J (J = 2,3,4,5, and 6). PL excitation spectra of Tb doped ZrO_2coatings are characterized by broad band region from 250 nm to 350 nm with a maximum at around 280 nm originating from $4f^8 \rightarrow 4f^7 5d^1$ transition of Tb^{3+} ions. The evolution of PL emission spectra shows that with increasing PEO time, i.e. increasing concentration of Tb in coatings, sharp emission bands of Tb^{3+} increase, while PL intensity of broad emission band of ZrO_2 host decreases. These results indicate the existence of energy transfer from ZrO_2 host to Tb^{3+} dopant.

1. Introduction

In the past few decades, researchers have invested considerable effort in studying the luminescence of rare-earth ions in different host matrices concerning practical applications such as advanced lighting, displays, and detection systems [1–4]. Trivalent rare-earth ions feature intense visible light emission as a consequence of 4f–4f transitions which are barely sensitive to the ion's surroundings due to the shielding effect of outer 5s and 5p shell electrons [5]. Of many trivalent rare-earth ions, terbium ion Tb^{3+} is particularly interesting because Tb^{3+} shows green emission which is one of three primary colors. Furthermore, its sharp green emission at around 544 nm is close to the optimal standards required for the green component of the tricolor [6].

ZrO_2 is frequently used as a host matrix for rare-earth ions due to intrinsic high refractive index, large optical band gap, high transparency in the visible and near-infrared regions, low optical loss, good chemical and photo-chemical stability, excellent mechanical properties, and low phonon energy (~ 470 cm^{-1}) [7–10].

An assortment of techniques has been utilized to prepare Tb^{3+} doped ZrO_2 materials such as spray pyrolysis [11,12], solvothermal method [13], combustion synthesis process [14,15], anodization [16], sol–gel dip coating technique [17], hydrothermal process [18], complex polymerization method [19], etc. In this work, we have used plasma electrolytic oxidation process (PEO) for the formation of ZrO_2:Tb^{3+} coatings.

PEO is a high-voltage anodizing process which produces stable oxide coatings on the surface of certain metals and their alloys [20]. Unlike the case of classical anodization, PEO processing is coupled with the formation of micro-discharges over the metal surface. Occurrence of a mixture of plasma-chemical, thermal, and anodic oxidation processes at the micro-discharge sites is related to the increased local temperature (10^3 K to 10^4 K) and pressure (~ 10^2 MPa) modifying the structure, composition, and morphology of obtained oxide coatings [21]. PEO coatings contain crystalline and amorphous phases where constituent species can originate both from metal and electrolyte.

Our recent investigation has shown that PEO processing is a suitable technique for incorporation of rare-earth oxide particles into ZrO_2 coatings formed on zirconium substrate [22,23]. The aim of this work is to examine the possibility of the formation of Tb^{3+} doped ZrO_2 coatings by PEO of zirconium in the electrolyte containing Tb_4O_7 particles and

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to investigate their photoluminescence (PL) properties. We assumed that conditions which exist at micro-discharging sites during the PEO allow the incorporation of Tb from electrolyte into ZrO_2 coatings.

2. Experimental details

Zirconium samples (99.95% purity, Alfa Aesar) were sealed with insulation resin leaving only active surface of 15 mm × 10 mm accessible to the electrolyte. The experimental setup used for PEO is described in Ref. [24]. PEO was carried out in DC regime at current density of 150 mA/cm^2. Water solution of 8 g/L $Na_3PO_4{\cdot}12H_2O$ was used as a supporting electrolyte. Commercially available Tb_4O_7 powder was added to supporting electrolyte in various concentrations up to 4 g/L. During the PEO, the temperature of the electrolyte was maintained at (10 ± 1) °C. After the PEO, samples were rinsed in distilled water to prevent additional deposition of electrolyte components during drying.

Scanning electron microscope (SEM) JEOL 840 A equipped with X-ray energy dispersive spectroscopy (EDS) was used to characterize the morphology and chemical composition of formed PEO coatings. The crystallinity of PEO coatings was analyzed by X-ray diffraction (XRD), using a Rigaku Ultima IV diffractometer. Diffraction peaks observed on XRD patterns are identified using Rigaku PDXL 2 software and COD database. PL spectral measurements were taken on a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer at room temperature, with a 450 W xenon lamp as the excitation light source. The obtained spectra were corrected for the spectral response of the measuring system and spectral distribution of the Xe lamp.

3. Results and discussion

3.1. Morphology, chemical, and phase composition of PEO coatings

Top view SEM micrographs of the coatings obtained at various stages of PEO processing in supporting electrolyte with addition of 4 g/L Tb_4O_7 powder are shown in Fig. 1. The micrographs reveal a typical structure for coatings formed by PEO of zirconium featuring a number of different sized and shaped pores, cracks, and regions resulting from the rapid cooling of molten material [25]. Results of the EDS analyses of surface coatings in Fig. 1 are shown in Table 1. The main elements identified in obtained PEO coatings are Zr, O, and Tb and they are rather uniformly distributed in the coatings (Fig. 2). It is observed that concentration of Tb in obtained coatings increases with PEO processing time.

Fig. 3 shows SEM micrographs of polished cross-sections of PEO coatings. The average thickness of coatings are about 3.2 μm, 5.1 μm, 5.6 μm, 6.4 μm, 7.1 μm, and 7.4 μm for PEO processing time of 1 min, 3 min, 5 min, 10 min, 20 min, and 30 min, respectively. Thickness of the coatings increases with PEO processing time, but non-uniformly because the highest growth rate is in the early stage of PEO.

The XRD patterns of used Zr substrate, Tb_4O_7 powder and Tb doped ZrO_2 coatings formed after various PEO times are shown in Fig. 4. All peaks in the XRD pattern of Tb_4O_7 powder can be indexed to fluorite cubic structure of Tb_4O_7 with pronounced reflections from (111), (200), (220), and (311) planes [26]. Diffraction peaks corresponding to monoclinic phase (m) and tetragonal phase (t) of ZrO_2 are observed in XRD patterns of Tb doped ZrO_2 coatings. Also, diffraction peaks corresponding to Zr substrate are observed in XRD patterns due to penetration of X-rays through the porous surface layer and reflection from the substrate. Although the incorporation of Tb_4O_7 particles into PEO coatings is possible through the electrophoretic and micro-discharging mechanisms [27], diffraction peaks related to Tb_4O_7 were not detected. The main reason for this is probably the low concentration of Tb_4O_7 which is uniformly dispersed all over the coating's surface. Tb_4O_7 powder contains mixed Tb^{4+} and more stable Tb^{3+} oxidation states. At temperature above 1500 K conversion of Tb^{4+} to Tb^{3+} is observed [28], so locally high temperatures at the micro-discharge sites (~ 10^4 K) should favor this conversion, i.e., Tb incorporated into coatings during the PEO is in +3 oxidation state.

The content of monoclinic and tetragonal phases of ZrO_2 (Table 2) was calculated from the integrated intensities of monoclinic peaks $(11\text{-}1)_m$ and $(111)_m$ at 2θ angle of 28.2° and 32.1°, respectively and tetragonal peak $(101)_t$ at 2θ angle of 30.2° using the following equations [29]:

$$W_m = \frac{I(11-1)_m + I(111)_m}{I(11-1)_m + I(101)_t + I(111)_m} \quad (1)$$

$$W_t = 1 - W_m \quad (2)$$

where W_m represents the weight fraction of monoclinic phase and W_t represents the weight fraction of tetragonal phase of ZrO_2.

The crystallite size of monoclinic and tetragonal phases in the coatings was calculated using the Scherrer's equation of the strongest diffraction reflections of the $(11\text{-}1)_m$ and $(101)_t$:

$$D = \frac{K\lambda}{\beta \cos\theta}, \quad (3)$$

where D is the crystallite size in nm, $K = 0.9$, λ is the wavelength of the incident X-rays in nm, θ is the Bragg angle, and β is full width at half maximum in radians. Table 2 shows that the crystallite size of both monoclinic and tetragonal phases of formed coatings increases with PEO processing time.

At ambient pressure ZrO_2 has three equilibrium phases in different temperature zones: cubic, tetragonal, and monoclinic phases [30]. Monoclinic phase transforms into tetragonal phase by heating above 1170 °C, while subsequent heating results into transformation to cubic phase above 2300 °C, followed by melting at 2680–2700 °C. During the PEO processing, molten zirconium material flows out of the discharge channels contacting with surrounding low-temperature electrolyte and rapidly solidifies at coating/electrolyte interface. Thus, rapid solidification of ZrO_2 favors the formation of m-ZrO_2 [31] and predictably m-ZrO_2 is the main phase in the coatings formed by the PEO processing of zirconium. At the beginning of micro-discharging, both monoclinic and tetragonal phases coexist inside of the micro-discharge channels, while transformation of monoclinic to tetragonal phase occurs with prolonged life of a micro-discharge [32]. In this stage of PEO small micro-discharges are evenly distributed over the surface [31] and provide enough energy to generate a high concentration of defects, such as oxygen vacancies, which could lead to the stabilization of the tetragonal phase [33]. However, prolonged PEO processing time restricts the transformation of monoclinic to tetragonal phase and the content of tetragonal phase gradually reduces after 1 min [34]. Namely, the number of micro-discharges decreases [31] and low local temperature around the micro-discharging sites favors the formation of monoclinic phase of ZrO_2 [33]. It is reported that rare earth elements, including Tb, stabilize tetragonal ZrO_2 phase at low temperatures [35]. After about 10 min of PEO process in supporting electrolyte with addition of 4 g/L Tb_4O_7 powder, the concentration of Tb incorporated in ZrO_2 coatings is high enough to stabilize its tetragonal phase. On the other hand, inspection of XRD patterns of ZrO_2 coatings formed after various PEO times in supporting electrolyte without Tb_4O_7 powder (Fig. 5a) shows that monoclinic ZrO_2 coatings are formed, except in the initial phase of the PEO process where the tetragonal ZrO_2 phase is also present. Fig. 5b shows XRD patterns of Tb doped ZrO_2 coatings formed after 10 min in supporting electrolyte with addition of Tb_4O_7 powder in different concentration. Evidently, the concentration of Tb in supporting electrolyte and, consequently, in ZrO_2 coatings has an effect on the crystal phases of samples and the content of tetragonal ZrO_2 phase increases with increasing concentration of Tb incorporated into coatings.

3.2. Photoluminescence of PEO coatings

PL of Tb doped ZrO_2 coatings originates from ZrO_2 host and